Supplementary File

Porous Polymer Monoliths Functionalized with C60 Fullerene for Highly Efficient Separations of Small Molecules

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Chemicals and Materials. Glycidyl methacrylate (GMA), ethylene dimethacrylate (EDMA), butyl methacrylate (BuMA), 2-hydroxyethyl methacrylate (HEMA), cyclohexanol, 1-dodecanol, 1-propanol, 1,4-butanediol, azobisisobutyronitrile (AIBN), 3-(trimethoxysilyl)propyl methacrylate, sodium hydroxide, isopropanol, uracil, benzene, toluene, ethylbenzene, propylbenzene, butylbenzene, pentylbenzene, chlorobenzene, glacial acetic acid and hydrochloric acid were obtained from Sigma-Aldrich (St. Louis, MO, USA). HPLC grade tetrahydrofuran, acetonitrile, ethanol, methanol, acetone and chloroform were obtained from EMD Chemicals (Gibbstown, NJ, USA). Thionyl chloride (99+%) was obtained from Alfa Aesar (Ward Hill, MA, USA). Prior to use, EDMA, GMA, BuMA and HEMA were first purified by passing them through activated alumina (activated, basic, Brockman I, 150 mesh) or by using monomethyl ether hydroquinone inhibitor removing beads (Sigma-Aldrich). Water was purified by a Nanopure Water System (Barnstead, Chicago, IL, USA) and filtered through 0.20 μm nylon membrane filters (Millipore, Bedford, MA, USA) prior to use.

High purity nitrogen (99.99%) was from Praxair (San Jose, CA) and was passed through a desiccant prior to use.

Polyimide-coated fused silica capillaries (375 μm o.d.× 100 μm i.d.) were purchased from Polymicro Technologies (Phoenix, AZ, USA). Phenyl-C61-buryric acid methyl ester from Nano-c (Westwood, MA, USA) and fullerene-C60 (99.9% sublimed) from Sigma-Aldrich were used as received. Flash chromatography was carried out in columns using Merck Kieselgel 60 (230-400 mesh) silica from Sigma-Aldrich. Molecular sieves (4 Å beads, 8-12 mesh, Sigma-Aldrich) were dried in an oven at 190 ^{o}C for at least 5 days before being used as drying agents.

Instrumentation. A nanoAcquity UPLC system (Waters, Milford, MA, USA) consisting of a binary solvent pump, sample manager, autosampler, and TUV detector equipped with a 10 nL cell was used for the separations. An external 10 nL injector with an electric actuator (CN4, Vici Valco Instruments, Houston, TX, USA) was used for sample injections. IR spectra were acquired using a Spectrum One IR (Perkin Elmer, Waltham, MA, USA) with a horizontal attenuated total reflectance (HATR) assembly. UV spectra were acquired using a Cary 5000 UV-Vis NIR spectrophotometer (Agilent, Santa Clara, CA, USA). Nitrogen adsorption/desorption isotherms were measured using a Micromeritics ASAP 2010 surface area and porosimetry analyzer (Norcross, GA, USA) and used for the calculation of the surface areas. A Gemini Ultra Field-Emission Scanning Electron Microscope (SEM, Zeiss, Peabody, MA, USA) was used for all SEM imaging. Fullerene containing compounds were characterized by ^{1}H NMR (500 MHz) and ^{13}C NMR (100 MHz) on a Bruker AV-500 and AVB-400 instrument, respectively. Matrix assisted laser desorption/ionization mass spectrometry (MALDI-TOF MS) was performed on a PerSeptive Biosystems Voyager-DE using 2,2':5',2"-terthiophene as the matrix.

Synthesis of [6,6]-phenyl C_{61} butyric acid ($PC_{61}BA$). All air and moisture sensitive reactions were performed under an inert atmosphere. Typically, 1 g [6,6]-phenyl C_{61} butyric acid methyl ester was dissolved in 50 mL chlorobenzene present in a 100 mL pressure tube containing an egg-shaped stir-bar. Then, 10 mL glacial acetic acid and 8 mL concentrated hydrochloric acid were added. The pressure tube was capped and placed in an oil-bath, heated to 95 °C, for 36 h. The biphasic mixture was vigorously stirred throughout the reaction. After allowing the reaction mixture to cool to room temperature, the contents of the pressure tube were poured, under stirring, into acetone (100 mL) while the stir-bar was kept in the tube with an external magnet. The precipitate was collected by filtration and washed well with acetone. After drying in a Buchner funnel, 778 mg of a crude product was obtained as dark brown powder and was used without further purification.

Synthesis of [6,6]-phenyl C_{61} butyric acid 2-hydroxyethyl methacrylate ester (PCB-HEM). $PC_{61}BA$ (0.778 g) was stirred in a mixture of 40 mL thionyl chloride and 20 mL chloroform at 55 °C for 4 h. Then the reaction continued at room temperature for a further 72 h. The liquids were removed under reduced pressure with mild warming in a water bath and the crude acid chloride was dissolved in 30 mL anhydrous toluene and 4 mL of 2-hydroxyethyl methacrylate added. This reaction mixture was left to stir at 40 °C for 20 h. After cooling to room temperature, the product was precipitated in 200 mL acetone. A small amount of water (~5 mL) was added in order to facilitate the precipitation. The product was filtered off and dissolved in 10 mL chloroform. This solution was loaded onto a silica gel column containing approximately 300 mL of silica and separation was carried out with chloroform as the mobile phase. The first eluting strong band was discarded, and the second band was collected as pure product. The fractions collected from the silica column were reduced to approximately 30 mL and precipitated in 170 mL methanol. Note: A sticky dark brown paste is obtained rather than a fluffy light brown powder if too much chloroform is present during this final precipitation. It is suggested that if a paste is obtained, all solvents be removed and the precipitation re-preformed. $PC_{61}B$-HEMA (340 mg) was obtained representing a yield of 31%. ^{1}H NMR (500 MHz, *$CDCl_3$*): δ (ppm) = 7.91-7.93 (m, 2H), 7.53-7.56 (m, 2H), 7.47-7.49 (m, 1H), 6.1 (m, 1H), 5.6 (m, 1H), 4.3 (m, 4H), 2.9-2.93 (m, 2H), 2.55 (t, J = 7.54 Hz, 2H) 2.15-2.25 (m, 2H), 1.95 (m, 3H), 1.54 (m, 2H). ^{13}C NMR (100 MHz, *$CDCl_3$*): (δ ppm) = 172.844, 148.816, 147.805, 145.878, 145.241, 145.204, 145.103, 144.840, 144.813, 144.712, 144.554, 144.475, 144.055, 143.805, 143.083, 143.043, 142.972, 142.219, 142.154, 141.042, 140.795, 138.070, 137.612, 135.962, 132.133, 128.498, 128.316, 126.191, 79.889, 62.440, 62.255, 51.869, 33.958, 33.678, 30.993, 22.360, 18.389. MALDI-TOF MS m/z = 1005.46. The material was kept away from direct light sources and stored in a dry box.

Activation of fused silica capillaries. An empty capillary was rinsed with acetone and water, flushed with 0.2 mol/L sodium hydroxide for 30 min at a flow rate of 0.25 µL/min using a syringe pump, and then rinsed with water. Next, 0.2 mol/L hydrochloric acid was pumped through the capillary for 30 min at a flow rate of 0.25 µL/min, followed by water and ethanol. A 20% w/w solution of 3-(trimethoxysilyl)propyl methacrylate in 95% ethanol with an apparent pH adjusted to 5 using acetic acid, was pumped through the capillary at a flow rate of 0.25 µL/min for 1 h. The capillary was then washed with acetone, dried in a stream of nitrogen, and left at room temperature overnight before use.

Effect of capillary filling on the efficiency and reproducibility of butyl methacrylate based monoliths. Although appearing trivial in nature, the method of filling the polymerization mixture into derivatized capillaries plays a significant role in column reproducibility. Figure S1 illustrates the effect of timing for filling capillaries after being removed from the sonicator. No matter what the efficiency is for the overall set of columns, an initial trend of increasing column efficiency is observed, reaching a maximum when the column is filled at 5 min after being removed from the sonicator. After 5 min, the efficiencies level off to a relatively constant value. Although PCB-HEM remains dissolved in the monomers for days after sonication, addition of the porogens to the monomers causes separation of the second phase and the solution appears cloudy, indicating that after removing the mixture from the sonicator, eventual precipitation and settling of the PCB-HEMA may occur. Re-sonicating the polymerization mixture rejuvenates the solution to undergo the same cycle. Dynamic light scattering measurement with PCB-HEM dissolved in the porogens demonstrates a dynamic change in average particle size of the precipitate with time after sonication, reaching a plateau size after about 6 min, that holds for several hours. Continually sonicating the mixture while filling the capillary columns affords reproducible columns (t_r and N RSD < 3.3%), but with only modest efficiencies, averaging 33,000 plates/m. To fully test the effect of presence of PCB-HEM on the formation of the monoliths, complete polymerization mixtures containing butyl methacrylate were filtered through 0.2 µm filters or left to settle overnight before being used. In both cases, the best efficiencies of the columns were 17,000-23,000 plates/m.

We also tested an alternate approach to filling the capillaries. Instead of using pressure of nitrogen to drive the mixture into the capillaries, the polymerization mixture was drawn into a standard 250 μL syringe. In contrast to aggregation and precipitation in a stabilized vial, the continual filling and pressing motion of the syringe promoted faster aggregation and settling rates of PCB-HEM without any orientation. This approach led to a large variability in both the morphology of monoliths and the column performance (RSD > 10%), with all the columns affording an efficiency of less than 20,000 plates/m.